A Comparison of Methods for Calculating Fast Electron-Transfer Rate Constants from Electron Spin Resonance Line Width Studies. Application to the Dibenzo-*p*-dioxin Cation System

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Abstract: The electron-transfer rate constant for exchange between the radical cation and the neutral precursor of dibenzo-*p*-dioxin (DBDO) has been determined from esr spectra in both the fast- and slow-exchange regions. Results from the simple formulas for calculating rate constants in the fast-exchange region are compared to those obtained using formulas applicable in the region of small broadenings. When corrections as suggested by Johnson and Holz are applied the two procedures give nearly identical rates. The simplicity of the DBDO cation esr spectrum also allowed a careful check of the statistical corrections necessary if one calculates rate constants from broadening of different hyperfine lines. Within experimental error different lines yield the same result if a statistical correction factor is applied. Our results provide the first experimental verification of the correctness of using either eq 1 or 2 of the text for esr electron-transfer studies in cation systems.

In recent years electron spin resonance (esr) has been used extensively to determine electron-transfer rates in organic anion systems,[2–12] whereas very little use of this technique has been directed to cation systems.[13] One may assume that, in either case, rate constants can be calculated in the region of small broadenings where the spectral hyperfine lines are well resolved, by the expression

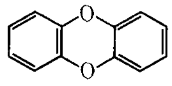
$$k = 1.52 \times 10^7 \Delta H/(1 - P_j)[\mathrm{c}] \tag{1}$$

where ΔH is the peak-to-peak increase in line width due to exchange (in gauss), [c] is the concentration of neutral diamagnetic material in moles per liter, and $1 - P_j$ is a correction for taking into account which hyperfine line is used; or, the fast-exchange region, where the spectral hyperfine lines are collapsed into one sharp Lorentzian line, by the expression

$$k = 2.04 \times 10^7 \nabla / \Delta H[\mathrm{c}] \tag{2}$$

where ∇ is the second moment of the unbroadened spectrum in gauss,[2] ΔH is the peak-to-peak corrected line width, and [c] has the same meaning as above. These two expressions are derived by applying limiting conditions to the full line-shape function for an N-site exchanging system.[14]

Due to the simplicity of the electron spin resonance spectrum of dibenzo-*p*-dioxin (I), we were able to obtain the second-order rate constant for electron exchange between the free cation radical and its neutral precursor from both the exchange-narrowed and exchange-broadened regions. We then compared results obtained using either the approach suggested by eq 1 or 2. In addition we wished to check the applicability of eq 1 for cationic systems as a follow-up to work performed by Zandstra and Weissman some years ago.[15] Solvent effects on the rate constant were also expected. Corrections suggested by Johnson and Holz[16] were applied to the fast-exchange data.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Experimental Section

1. **Materials.** Dibenzo-*p*-dioxin (DBDO) was commercially obtained and vacuum sublimed. Reagent grade chloroform was purified by removing the ethanol with concentrated H_2SO_4 and then washing several times with water. Distillation from P_2O_5 keeping the center fraction, followed by storage in a vacuum bottle over type 4A molecular sieves, completed its purification. Reagent grade acetonitrile was twice distilled from P_2O_5 and a center-cut portion was stored in a vacuum bottle over type 4A molecular sieves. Tetrabutylammonium perchlorate (TBAP) was used as commercially obtained.

2. **Preparation of Cations for Rate Studies.** Each positive ion solution for a rate experiment was prepared in a Pyrex apparatus under vacuum. The appropriate solutions were electrolytically oxidized, with 0.04 *M* TBAP as the supporting electrolyte, for a time sufficient and with a potential high enough so as to obtain the desired radical concentration. The sample apparatus was constructed so the anode and cathode compartments were separated by a fritted glass disk and the anode solution could be directed to an attached probe for experimental measurements.

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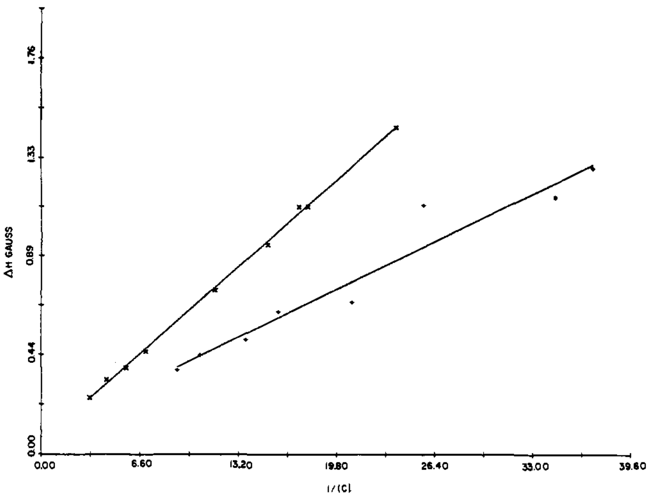

Figure 1. Least-squares plots of line width *vs.* reciprocal of DBDO concentration in moles per liter: (×) electrolytic oxidation in 3/1 $CHCl_3$–CH_3CN solvent mixture, 0.04 *M* TBAP; (+) electrolytic oxidation in CH_3CN solvent, 0.04 *M* TBAP.

3. Esr Spectrometer. All esr measurements described were made with a Jeolco-3BSX spectrometer operating near 9.7 kMHz, with linear field sweep and 100-kHz field modulation and equipped with a variable temperature cavity. Temperatures were maintained to ±1°. Calibration of the field sweep was achieved by using the 1.83-G esr splitting between lines 11 and 13, or 13 and 15, of a dimethoxyethane solution of naphthalenide ion.

4. Corrections. Line shapes of selected spectral lines were examined[17] and all found to be very nearly Lorentzian. Spin concentrations of selected samples were examined by comparisons with standard 1,1-diphenyl-2-picrylhydrazyl (DPPH) samples in similar solvents and an upper limit of 10^{-4} *M* cation was found in all cases (usually the spin concentration was less), thus suggesting no large corrections were necessary for Heisenberg broadening. If necessary, modulation corrections were made.[18]

Results

A. Fast-Exchange Region. The second-order rate constant in the fast-exchange region was obtained in both CH_3CN and 3/1 $CHCl_3$–CH_3CN solvents. In order to obtain these rate constants from the plot of the peak-to-peak line width *vs.* the reciprocal of the molar concentration of neutral DBDO (Figure 1), one must obtain the second moment of the uncollapsed hyperfine spectrum. The five-line hyperfine spectrum of the DBDO positive ion has been reported[19] (DBDO oxidization in H_2SO_4 with a trace of H_2O_2 present). A proton coupling constant of 2.52 G was reported for this system (interaction with four equivalent protons). In this laboratory, electrolytic oxidation in CH_3CN and 3/1 $CHCl_3$–CH_3CN solvents yielded coupling constants of 2.10 and 2.14 G, respectively. The second moments obtained were 4.58 (3/1 $CHCl_3$–CH_3CN) and 4.41 G^2 (CH_3CN).

Table I shows the second-order rate constant and intercept obtained from Figure 1. (See below for significance of the intercept.)

Figures 2 and 3 show the temperature dependence of the rate constants for the two systems. The apparent activation energies obtained from Figures 2 and 3 are shown in Table I.

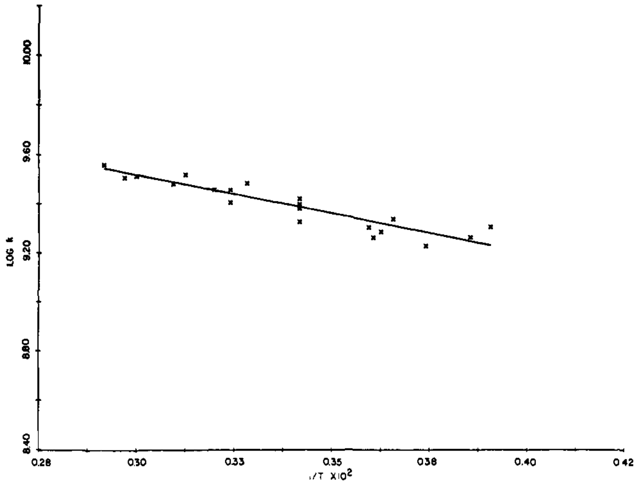

Figure 2. Least-squares activation energy plot for DBDO in CH_3-CN solvent.

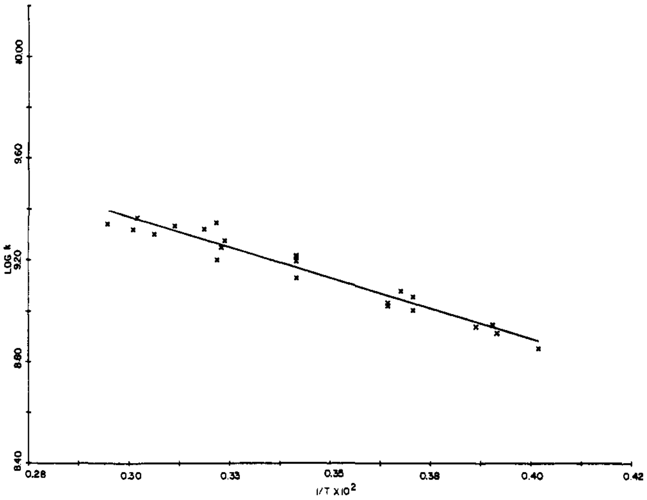

Figure 3. Least-squares activation energy plot for DBDO in 3/1 $CHCl_3$–CH_3CN solvent mixture.

Table I. Rate Constants, Activation Energies, and Intercepts[a,b]

$DBDO^+$/DBDO	$10^{-9}k$, M^{-1} sec^{-1}	E_A, kcal	*I*, G
CH_3CN	2.74 ± 0.44	1.51 ± 0.31	0.09 ± 0.09
3/1 $CHCl_3$–CH_3CN	1.58 ± 0.25	2.29 ± 0.47	0.05 ± 0.03

[a] Temperature 18°. [b] Rate constant and activation energy errors are computed estimates; intercept errors are standard deviations from the mean.

B. Theoretical Restrictions of the Simple Fast-Exchange Treatment. Johnson and Holz[16] have made an analysis of the theoretical restrictions on obtaining rate constants using eq 2. Among the criteria which they stated for eq 2 to be valid were (1) linearity of ΔH *vs.* 1/[c] plot; (2) intercept of ΔH *vs.* 1/[c] should yield a reasonable value of the natural line width in the absence of exchange; (3) Lorentzian line shape of the collapsed spectral line. These criteria have all been met by this system. (Admittedly, experimental errors in this type of work are great enough to mask any slight nonlinearity and any small deviation from Lorentzian line shape.)

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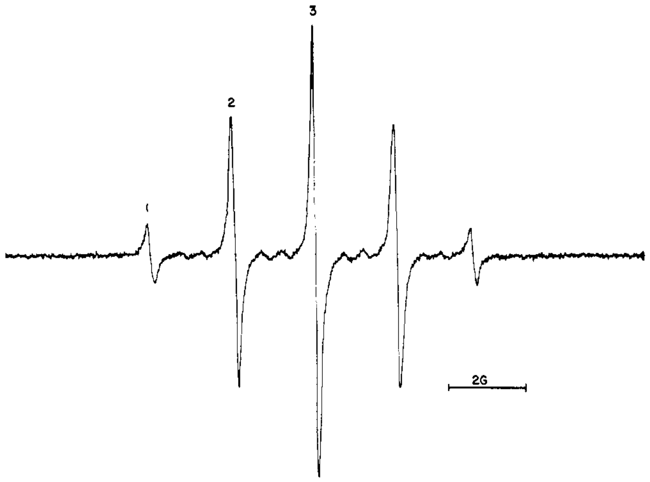

Figure 4. Hyperfine spectrum of $DBDO^+$ electrolytically oxidized in 3/1 $CHCl_3$-CH_3CN solvent mixture with 0.04 *M* TBAP.

A more stringent criterion for the use of eq 2 was developed by Johnson and Holz[16] and depends on the quantity given by eq 3.

$$Z = \sqrt{3}/2(\Delta H/\sqrt{\nabla}) \qquad (3)$$

Z is an experimentally obtained quantity where ΔH is the line width and ∇ is the second moment. It is a guide to determining whether the data used are within the exchange-narrowed region. Johnson and Holz found that the experimental data points of the ΔH *vs.* 1/[c] plot (eq 2) must have *Z* values less than 0.2 in order that the rate constant calculated will fall within the limit of 5% error. Table II gives *Z* values for DBDO in two solvent mixtures. As can be seen from Table II enough of the *Z* values are greater than 0.2 that the 5% error limit could not be met, or, according to Johnson and Holz[16], many of the points on the graph represented experiments not in the region of fast exchange.

Table II. Line Width and *Z* Values for DBDO Cation in Fast-Exchange Solutions

CH_3CN system		3/1 $CHCl_3$-CH_3CN system	
ΔH, G	*Z*	ΔH, G	*Z*
0.37	0.154	0.25	0.101
0.44	0.183	0.31	0.126
0.51	0.212	0.38	0.155
0.64	0.264	0.46	0.185
0.68	0.282	0.73	0.297
1.12	0.463	0.94	0.381
1.16	0.479	1.11	0.450
1.29	0.533	1.11	0.450
		1.47	0.596

In the same paper[16] a method was described which involves corrections utilizing the fourth moment of the uncollapsed hyperfine spectrum whereby one could correct results to the 5% error limit even though *Z* values were as large as 0.4, This method has been used on our data and the results are shown in Table III along with the rate constants obtained from eq 2 for comparison. Since Table II shows that, to a great extent, the *Z* values are close to or less than 0.4, this should be a more accurate way of treating the experimental data.

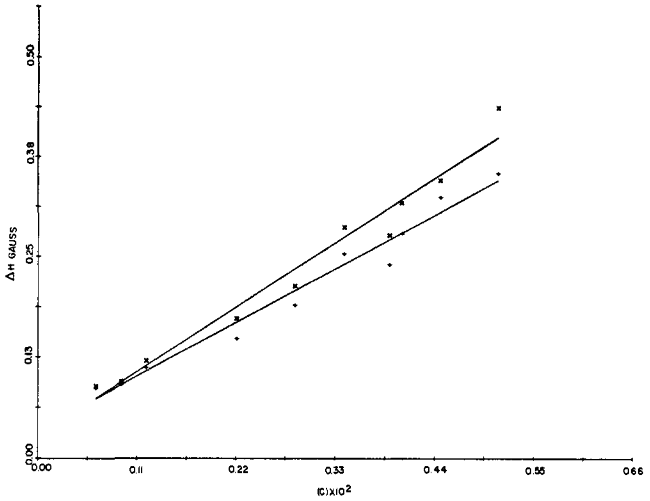

Figure 5. Least-squares plot of line width *vs.* DBDO concentration in moles per liter: electrolytic oxidization in 3/1 $CHCl_3$-CH_3CN solvent mixture with 0.04 *M* TBAP; (×) line 2, (+) line 3.

Table III. Rate Constants[a]

System	Uncor $10^{-9}k$, M^{-1} sec^{-1}	Cor[b] $10^{-9}k$, M^{-1} sec^{-1}
CH_3CN	2.74 ± 0.44	2.18 ± 0.35
3/1 $CHCl_3$-CH_3CN	1.58 ± 0.25	1.34 ± 0.22

[a] Errors are computed estimates. [b] Fourth moment correction applied.

C. Region of Small Broadenings. The second-order rate constant was obtained in this manner only in the 3/1 $CHCl_3$-CH_3CN solvent mixture due to the instability of $DBDO^+$ in pure CH_3CN at low concentrations of DBDO. The rate constant was obtained by observing lines 2 and 3 (see Figure 4) as varying amounts of neutral compound were present.

Due to instability we were unable to first generate the hyperfine spectrum and then add neutral DBDO to observe the broadening as is common in slow exchange work.[2a] Instead we prepared samples with the desired neutral DBDO concentrations and then, with considerable care, oxidized the desired amount of DBDO in each sample. Then, instead of using the peak-to-peak line width due to exchange, which is the total line width minus the line width of the unbroadened line, we used the total peak-to-peak width as the plotted variable *vs.* the molar concentration of neutral DBDO (see Figure 5). The intercept gave a reasonable value of the natural line width. Table IV gives the rate constant and intercept obtained from the two resonance lines using eq 1.

Table IV. Statistical Factor, Rate Constant, and Intercept[a,b]

Spectral line	$1 - P_j$	$10^{-9}k$, M^{-1} sec^{-1}	*I*, G
Line 2	0.750	1.50 ± 0.24	0.03 ± 0.02
Line 3	0.625	1.50 ± 0.24	0.04 ± 0.02

[a] Temperature 18°. [b] Rate constant errors are computed estimates; intercept errors are standard deviations from the mean.

Discussion

A. Fast Exchange. By observing the corrected and uncorrected rate constants in Table III it can be seen that the Johnson and Holz correction lowers the calculated rate constant. This is reasonable, since, as the electron exchange in a solution of radicals and neutral precursor approaches the limits of the exchange narrowed region, *i.e.*, it approaches the intermediate region where complete averaging of the nuclear spin states is not obtained, less broadening of the line occurs than would be normally expected. The abnormally small esr line width in this region would cause the appearance of nonlinearity in the ΔH *vs.* 1/[c] plot; however, due to experimental error the nonlinearity could be masked and the least-squares fit of the ΔH *vs.* 1/[c] plot would give a low value for the slope. Thus if data from these borderline cases is used, a high second-order rate constant would be obtained by using eq 2. The correction suggested in ref 16 tends to correct for this error.

The expression[20] ($\ln k \propto 1/D$) predicts an increase in rate with a decrease in the bulk dielectric constant for reactions between ions and neutral molecules. Also the dielectric constants of the solvents involved (CH_3CN, $D = 38.0$, and $CHCl_3$, $D = 4.8$)[21] suggest that the bulk dielectric constant of system 2 (3/1 $CHCl_3$–CH_3CN solvent mixture) is less than that of system 1 (CH_3CN solvent). This would tend to contradict our results of higher rate in the higher bulk dielectric constant system. But, at sufficiently low dielectric constants (as in system 2), substantial ion pairing with ClO_4^- could become important. The smaller rate constant and higher activation energy for system 2 and the reverse for system 1 strongly suggests the presence of ion pairing in system 2.

Other authors[5,6,9,10b,22] have observed rate variations in anion systems which they attribute to ion pairing between the organic anion and the alkali metal cation. Ahn and Johnson[23] have even suggested a type of ion pairing between the *N,N*-dimethylpyrazine cation and the tetrafluoroborate anion to help explain the line shapes of the esr spectrum of the cation radical. The affinity of aromatic amine cations and perchlorate anion has been suggested by reports[24–26] of the formation of amminium perchlorate salts. Thus some type of association between ClO_4^- and DBDO$^+$ is plausible in a low dielectric constant medium.

B. Slow Exchange. Extreme care was taken in preparing the samples for the slow-exchange study. The samples were compared to DPPH samples of the same solvent mixture to ensure that an upper limit of 10^{-4} *M* DBDO$^+$ concentration was not exceeded. If a higher DBDO$^+$ concentration had been produced, besides introducing Heisenberg broadening, errors due to a decrease in the neutral DBDO concentration would also have resulted. This latter consideration would be quite important since in some of these samples the neutral DBDO concentration is of the same order as the DBDO$^+$ concentration.

Besides obtaining the second-order rate constant for the DBDO$^+$ system in the slow-exchange region, we also checked the validity of the correction factor ($1 - P_j$) in eq 1 for cation systems. Zandstra and Weissman's classic study[15] of the naphthalenide–naphthalene system to determine whether only those processes in which the resonant frequencies of the electron spin in its initial and final states are different contribute to broadening has been our guide. They stated that if the electron spin undergoes a transfer process which is characterized by a mean residence time in a particular molecule, then the residence time in a nuclear spin arrangement which yields the *k*th line is

$$1/t_k = 1/t[1 - P_j] \qquad (4)$$

where t_k is the time between changes of resonance frequency and the term $1 - P_j$ is the probability of an electron finding itself interacting with a particular nuclear quantum state.

If the electron-transfer rate is independent of initial and final nuclear spin states and if any magnetic pulse during transit is small, the above equation should give the relative broadening of the separate spectral lines. They[15] found that, by applying the $1 - P_j$ correction to eq 1, they obtained the same rate constant within experimental error from any of the spectral lines in the naphthalenide–naphthalene system.

The requirement that the pulse during transit be small is reasonable for organic anion systems because in the process of transfer the electron is imagined to jump between antibonding orbitals. Pairing and unpairing of electron spins is thus not a factor in the physical process of the electron jump.

In cation systems the electron transfer is to and from filled bonding or nonbonding orbitals and the electron spins must pair and unpair in the electron-transfer process. The present study has been made in this laboratory to investigate whether the possibility of sufficiently strong pulses during transit due to the spin pairing and unpairing could occur for cation exchange. If such pulses could occur, eq 4 would then not adequately account for the broadening of all the spectral lines. One would suspect different rate constants to be calculated from data for broadening of different spectral lines. As can be seen from Table IV this is not the case since the correction $1 - P_j$ is adequate to yield the same calculated rate constant, within experimental error, from the different spectral lines in this system. This suggests strongly that there is not a sufficient disturbance due to spin pairing and unpairing to invalidate the assumptions behind eq 4 and thus also eq 1.

C. Comparison of Rate Constants. Tables III and IV give the second-order rate constants obtained from fast- and slow-exchange data for the 3/1 $CHCl_3$–CH_3CN solvent mixture system, and it shows that the corrected rate constant from the fast-exchange data and the rate constant from the slow-exchange data compare favorably within experimental error.

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Summary and Conclusion

We have determined rate constants for the DBDO$^{\cdot+}$ cation system in the fast- and slow-exchange regions and have obtained good agreement between individual experiments. We have also found smaller rate constants and higher activation energies in a lower bulk dielectric constant medium indicating that ion pairing between the organic cation and ClO_4^- is probable.

Slow-exchange studies have shown that the correction to the slow-exchange equation proposed by Zandstra and Weissman[15] for anion systems also applies to cation systems. The theoretical correction introduced by Johnson and Holz[16] which extends the usefulness of eq 2 has been applied to our fast exchange data and we have found that by applying this correction a lower rate constant was obtained, which is what would be expected since the Z values of several data points did exceed the limiting value.

Thus, we have shown that either eq 1 or 2 is generally valid to determine electron-transfer rate constants if appropriate corrections are made.

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Kinetics of Proton Transfer to Cyanines.[1] A Temperature-Jump Study

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Abstract: A linear free energy type relationship has been obtained between the logarithm of the measured protonation rate constants of a number of substituted 2,2′-cyanines and the change in π-electron delocalization energies as a consequence of protonation. The absolute values of all rate constants measured by the T-jump technique are five to seven orders of magnitude below diffusion controlled indicating that protonation occurs on the methine carbon. Proton-transfer rate constants to the carbon from second acid–base pairs have Brønsted plots that are strongly unsymmetrical about $\Delta pK = 0$ showing saturation behavior at negative ΔpK values. Activation energies for proton transfer to pseudoisocyanine are between 8 and 9 kcal/mol, and entropies of activation are strongly negative leading to relatively low Arrhenius factors. Solvent isotope effects measured as a function of temperature for proton transfer involving acetic acid and pseudoisocyanine are large (~6). Kinetic salt effects support our assignment of relaxation times. Measurements in methanol–water solvents of varying dielectric constants suggest that the effective reaction distance for proton transfer may be relatively short. Thermodynamic parameters for proton transfer involving pseudoisocyanine are presented.

The 2,2′-cyanine compounds represent an interesting class of carbon acids whose acidities are known to vary directly as a function of changes in their π-electron delocalization energies[2] resulting from the difference in conjugation between the acid and conjugate base forms. To our knowledge there exists no kinetic study in the literature with respect to proton transfer to and from the methine carbon. The ultimate goal of such a study would be the understanding of the mechanism of proton transfer to aromatic carbon acids and the factors that determine the magnitude of the transfer rate constants. The limiting rates of proton transfer to carbon acids cover a range that is generally below the diffusion controlled limit characteristic for oxygen and nitrogen acids.[3] The main reasons given for the lowering of the rates of protonation of carbon acids include relatively weak hydrogen bonding between the carbon acceptor site and solvent molecules and the occurrence of molecular and electronic structure changes upon protonation.[3] The 2,2′-cyanines represent systems for which such assertions can be tested directly. Changes in the π-electron energies can be readily achieved by protonation and the electron densities can be calculated by conventional methods. Thus a direct correlation between the calculated polarity of the methine carbon in the substituted compounds and the dynamics of its protonation will be possible.

The protonation equilibria of the 2,2′-cyanines can be represented by the example of pseudoisocyanine

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[1] (a) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968. (b) In partial fulfillment of the requirements for the M.S. degree of P. J. Dynes, University of Southern California, 1969.

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